



CARBONYLATION AND HYDROFORMYLATION

Dr. Dario Cambié

Max Planck Institute of Colloids and Interfaces

Biomolecular Systems

Dario.Cambie@mpikg.mpg.de



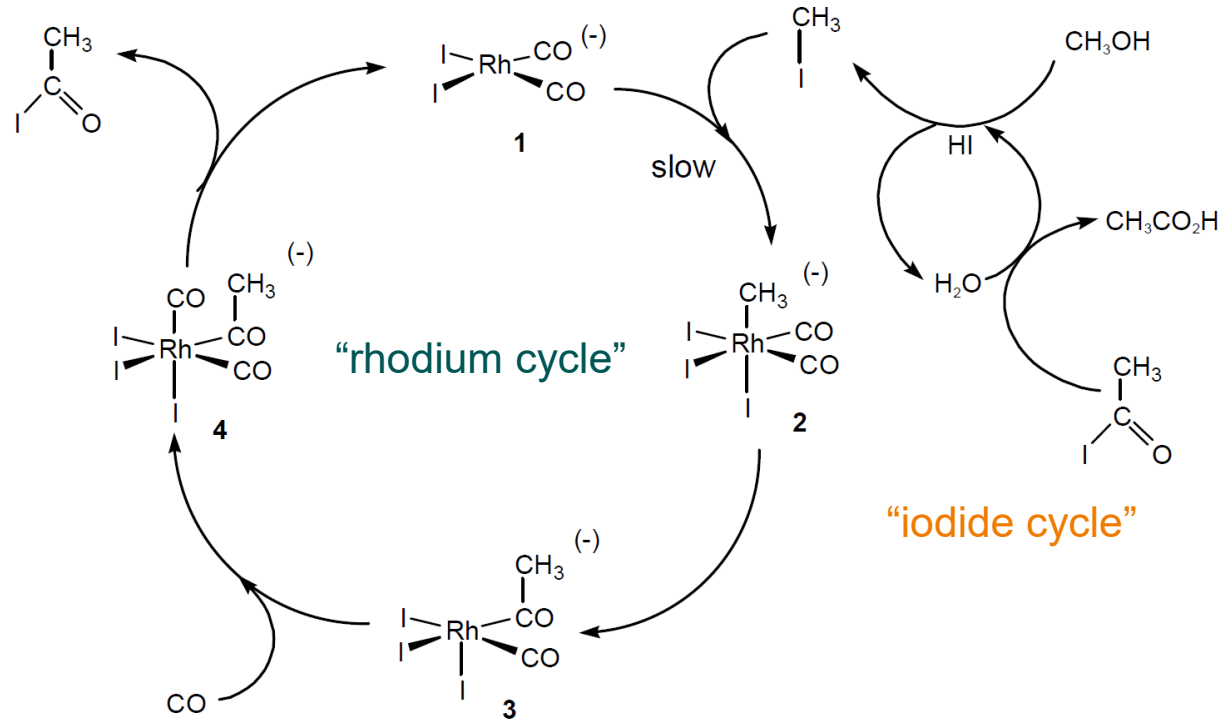
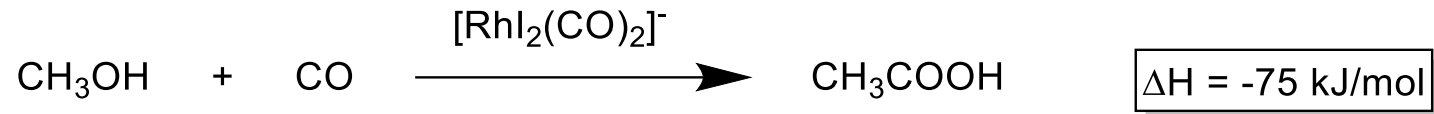
6.1 METHANOL CARBONYLATION

- CO as C1 feedstock + MeOH (from syngas) to synthesize acetic acid
- One of the largest homogeneous cat application (≈ 18 Mt/a, 85% Monsanto+Cativa processes)
- Rh/Ir (or any group 9 and 10 metal)

	BASF	Monsanto	BP Cativa™
Ind. introduction	1960	1970	1995
Temp	250 °C	150-200 °C	180 °C
P (bar)	600-700	30-60	30-40
Selectivity (vs. MeOH)	90 %	99 %	99.5 %
Selectivity (vs. CO)	70 %	90 %	> 94 %
Side-products	CH ₄ , CO ₂ , EtOH, MeCHO, EtCOOH	CH ₄ , CO ₂ , H ₂	Negligible



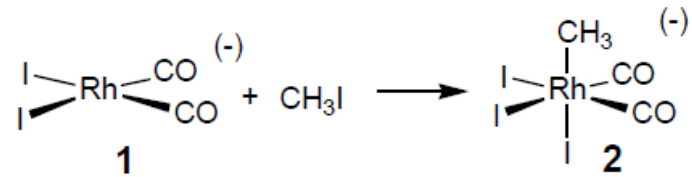
6.1.1 MONSANTO PROCESS - MECHANISM



- MeI OA is turnover determining step
migratory insertion, CO coordination and RE fast
- **1** is resting state, only CO species detected by IR



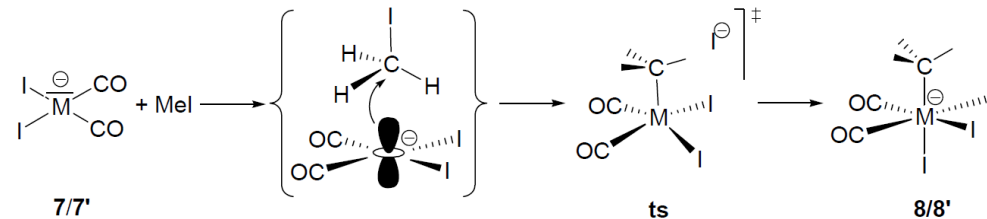
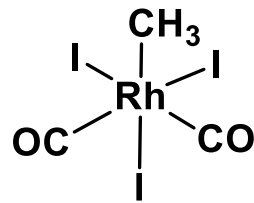
6.1.1 POD #1



^{13}C NMR: two equivalent carbons with $J_{\text{Rh-C}} = 60$ Hz

^{13}C NMR: methyl group with $J_{\text{Rh-C}} = 14$ Hz at $\delta = -0.6$ ppm

The structure of the metal complex below, resulting from the CH_3I oxidative addition in the rhodium-catalyzed methanol carbonylation, had been hypnotized from the 1960s. However, it was observed spectroscopically for the first time only in 1991. **Suggest a way increase its concentration in the catalytic cycle to make it detectable.**



- *OA via $\text{S}_{\text{N}}2$ -type mechanism on square planar $d8$ $\text{Rh}(I)$ complex, $k \propto [\text{MeI}]^*[\text{Rh}]$, MeI as solvent.*

Based on the considerations above, **suggest a way to accelerate the turnover-determining oxidative addition of MeI to $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ in the rhodium-catalyzed methanol carbonylation.**

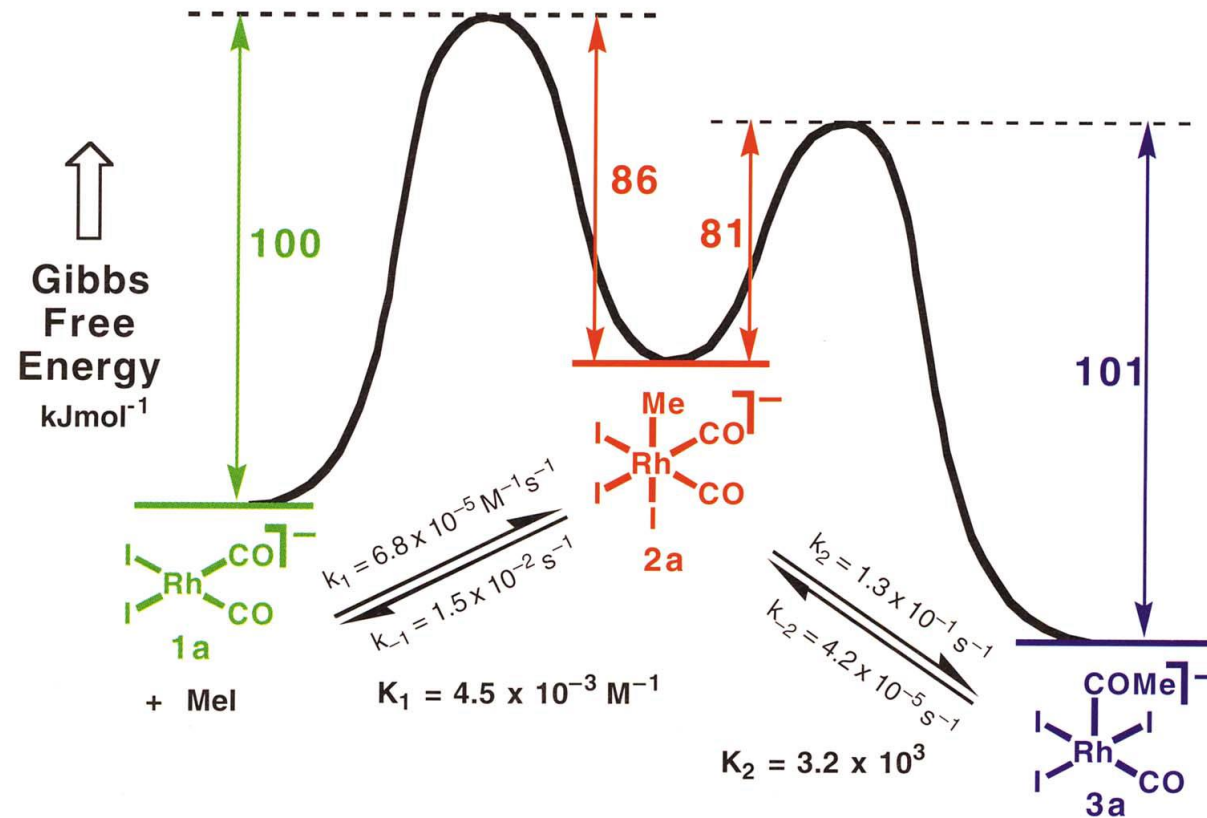
- *Increasing e -density via ligands (e.g. PR_3) However, stronger Rh-CO bond slows down insertion. Ligand design also needs to balance long-term stability... Not a solved problem!*

Maitlis, *JACS* **1991** 113, 22, 8567. DOI: [10.1021/ja00022a079](https://doi.org/10.1021/ja00022a079).

Thomas, *Coord. Chem. Rev.* **2003**, 243, 125. DOI: [dsd9ht](https://doi.org/10.1016/S0010-8546(03)00091-7)



6.1.1 MONSANTO PROCESS - MECHANISM



J. Chem. Soc., Dalton Trans. **1996**, 2187. DOI: [10.1039/DT9960002187](https://doi.org/10.1039/DT9960002187)



6.1.1 MONSANTO PROCESS – PROCESS SCHEME

kinetics OA turnover limiting,
matches overall reaction rate
-> independent of conversion,
good for process (higher
conversion, easier separation)

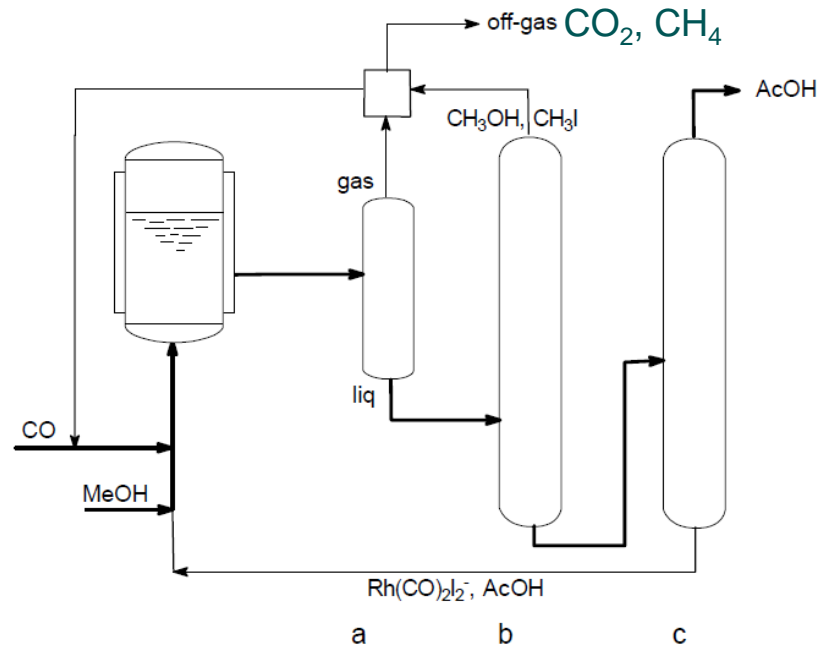


Figure 6.4. Process scheme Monsanto a= depressurisation, b= light ends removal, c= acetic acid distillation

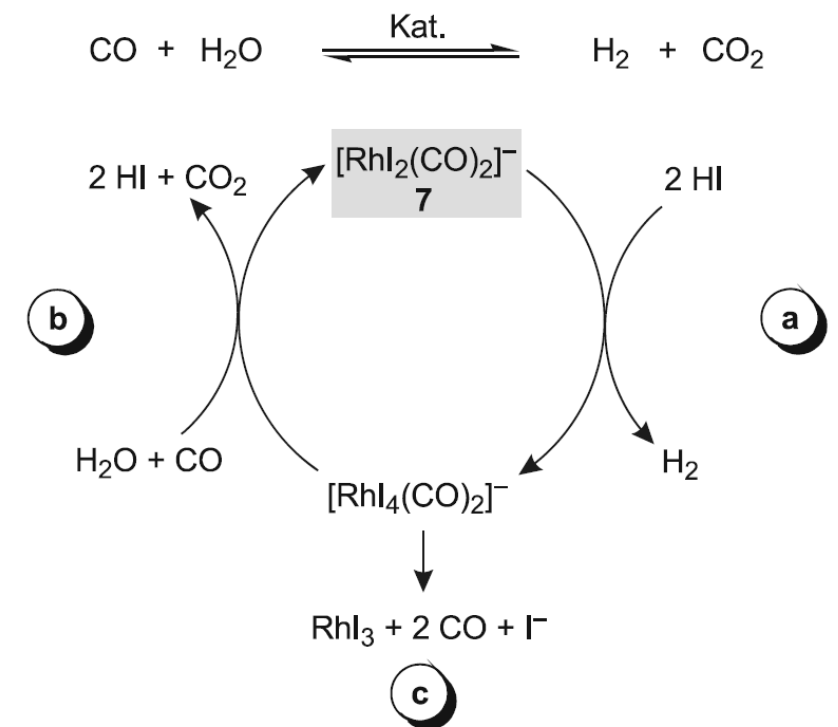
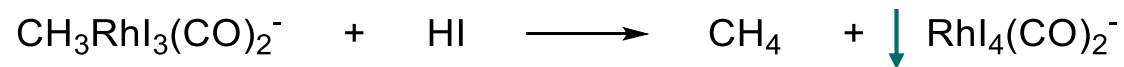


6.1.1 MONSANTO PROCESS – BY-PRODUCTS

- Rh complex like $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ also catalyze the **water-gas shift reaction**



- This consumes CO but enables to recover inactive Rh(III):





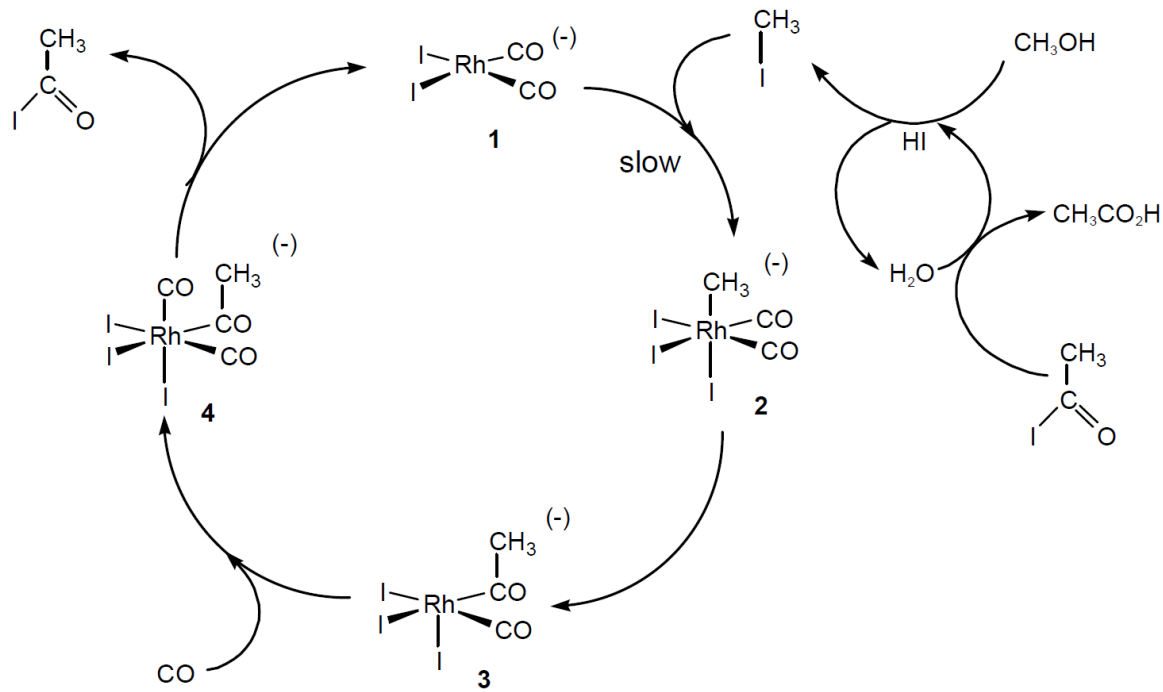
6.1.1 EASTMAN ACETIC ANHYDRIDE PROCESS

- From 1983, several 100 kton/a
- Similar to Monsanto but anhydrous conditions :D
and Rh(III) reduction? 5% H₂ added to CO stream
- Acetic acid replaces water, methyl acetate replaces methanol, Lil replaces HI

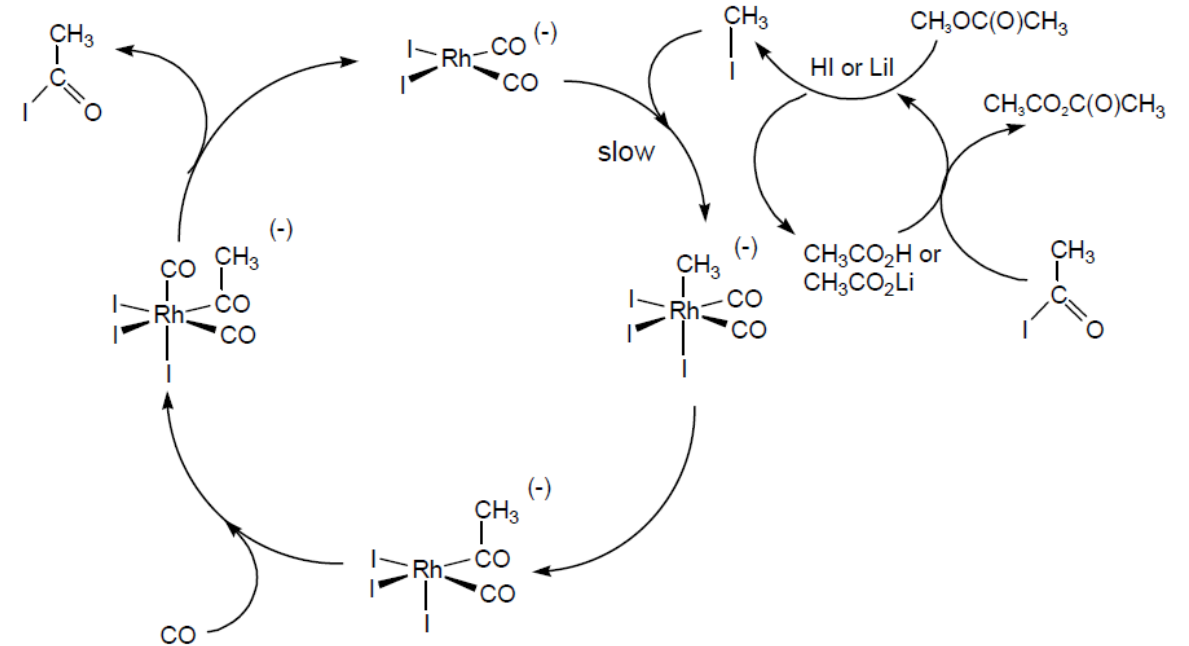


6.1.1 EASTMAN ACETIC ANHYDRIDE PROCESS VS. MONSANTO

Acetic acid - Monsanto



Acetic anhydride - Eastman





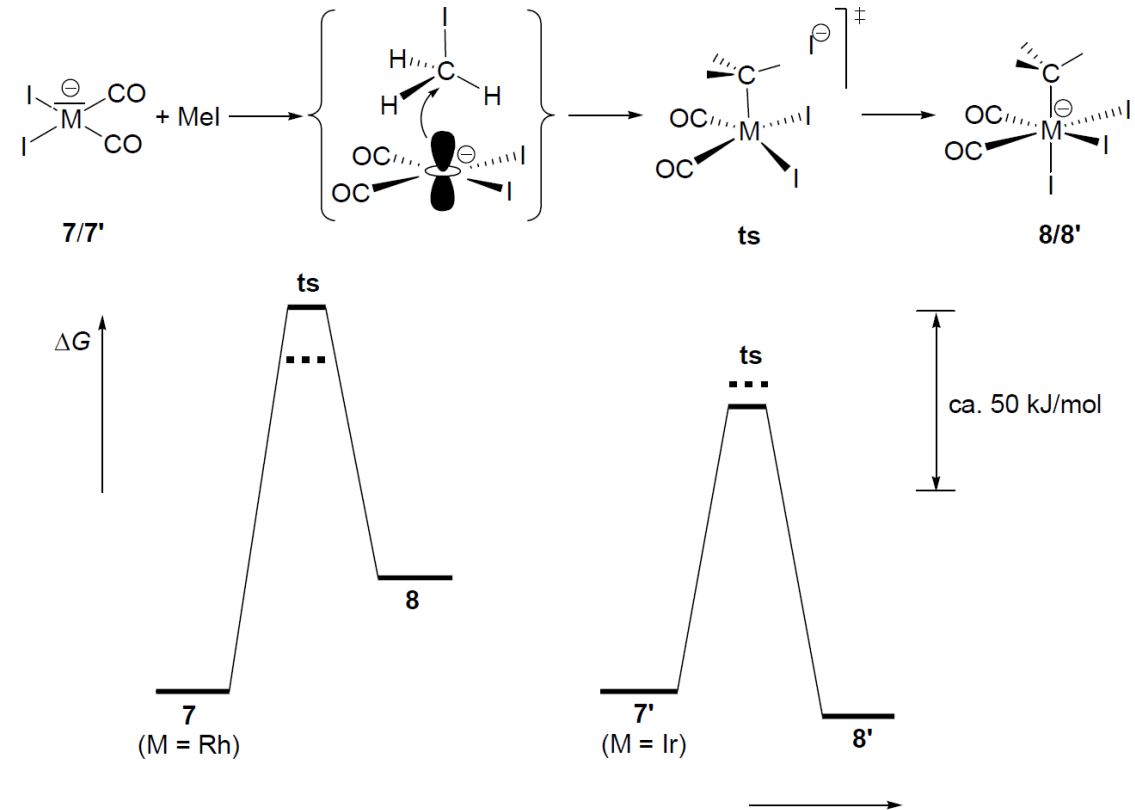
6.1.2 BP “CATIVA™” PROCESS – REPLACING Rh WITH Ir

- 25% times faster than Monsanto (under industrial process conditions, cat cycle kinetics up to 5x faster)
- Ir instead of Rh (actually cheaper despite 3rd row)



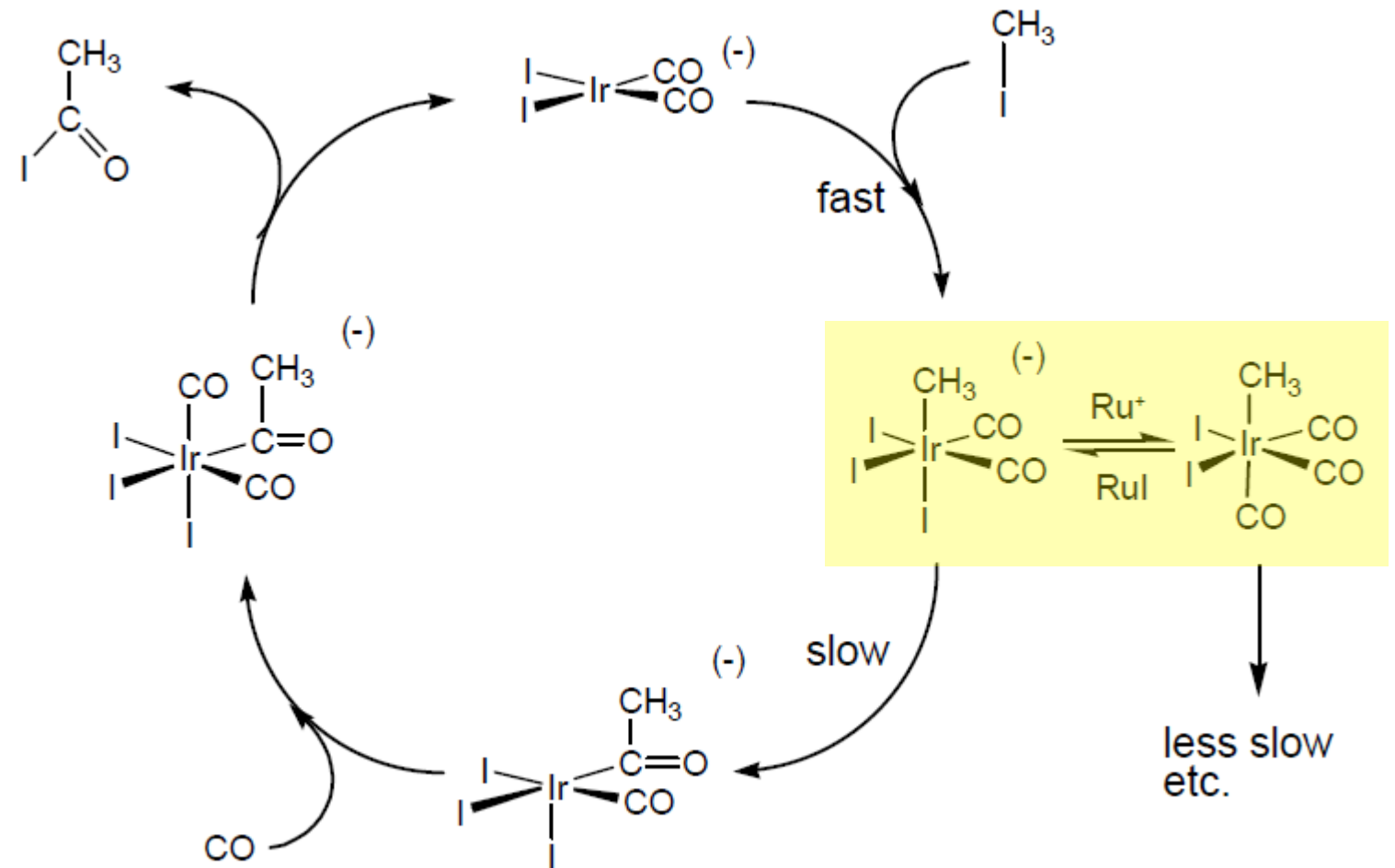
6.1.2 BP “CATIVA™” PROCESS – REPLACING Rh WITH Ir

- OA of MeI to $[\text{Ir}_2(\text{CO})_2]^-$ is 150 times faster than to $[\text{Rh}]$, no longer turnover determining step!
(because Ir-C stronger than Rh-C)
- However, migratory insertion slower! :(
New catalyst resting state is after OA
(Ru promoters)



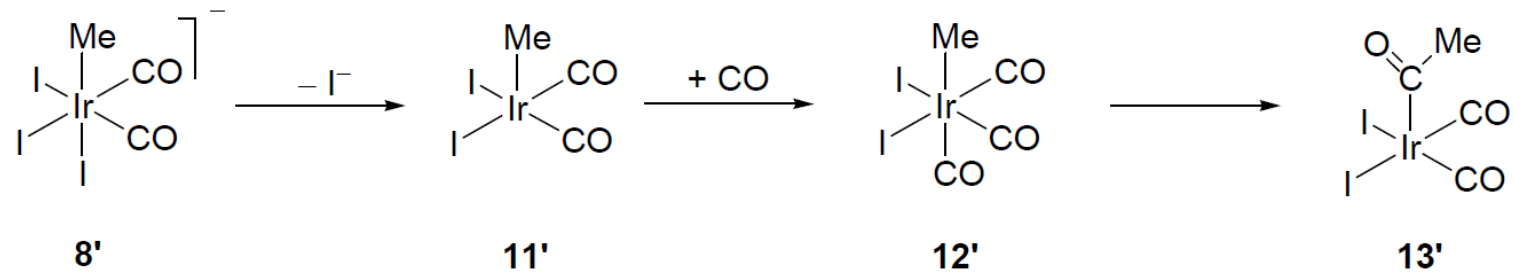


6.1.2 BP “CATIVA™” PROCESS – MECHANISM



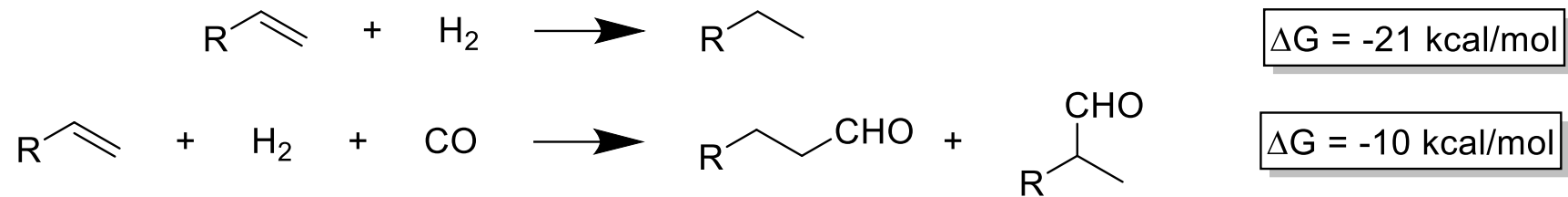


6.1.2 BP “CATIVA™” PROCESS – MIGRATORY CO INSERTION

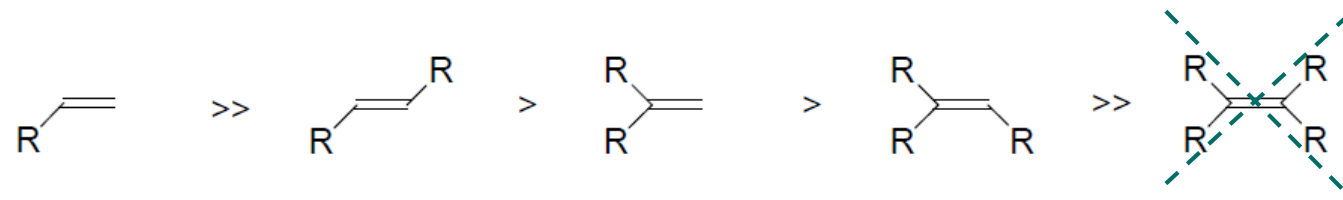




6.2 HYDROFORMYLATION (AKA “OXO SYNTHESIS”)



- 1938, Rolén at Ruhrchemie [Before at Kaiser-Wilhelm-Institut für Kohlenforschung w/ Fischer/Tropsch]
- Co/Rh, 2nd homogeneous catalysis process by scale after polymerization (12 Mt/a in 2008)
- Formal addition of HCHO across an alkene
- homologation from C_n to C_{n+1}
- Possible side reactions: hydrogenation, isomerization, aldehyde reduction...

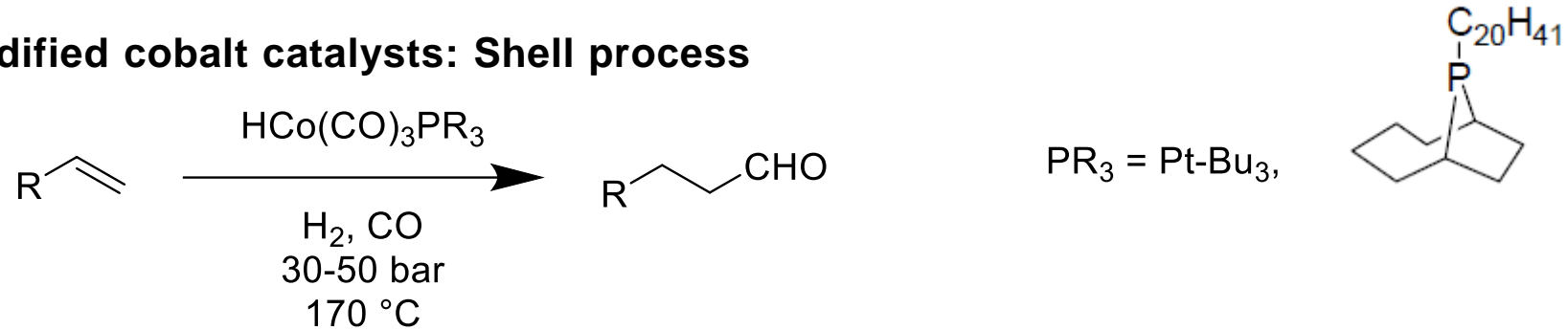


Otto Rolén biography: ACIE **1994** 33, 21, 2144. DOI: [10.1002/anie.199421441](https://doi.org/10.1002/anie.199421441)



6.2.1 COBALT-CATALYZED HYDROFORMYLATION - PHOSPHINES

Phosphine modified cobalt catalysts: Shell process



Advantages	Disadvantages
More stable cat, lower P_{CO} necessary, higher temperature possible	Lower reaction rate (stronger [M]-CO)
Higher linear:branched ratio	Higher P_{H_2}



6.2.1 COBALT-CATALYZED HYDROFORMYLATION - PHOSPHINES

Phosphine modified cobalt catalysts: Shell process

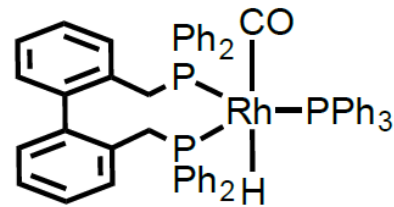
In Komplexen $[\text{CoH}(\text{CO})_{4-n}(\text{PR}_3)_n]$ gilt für $\text{PR}_3 = \text{P}(n\text{-Bu})_3$:

n	0	1	2	3
$T_{\text{Zers.}}$ (in °C)	-20	20	160	80
ν_{CO} (in cm^{-1})	2043–2121	1933–2050	1902–1978	1883
$\text{p}K_a$	1	7 ($\text{PR}_3 = \text{PPh}_3$)		



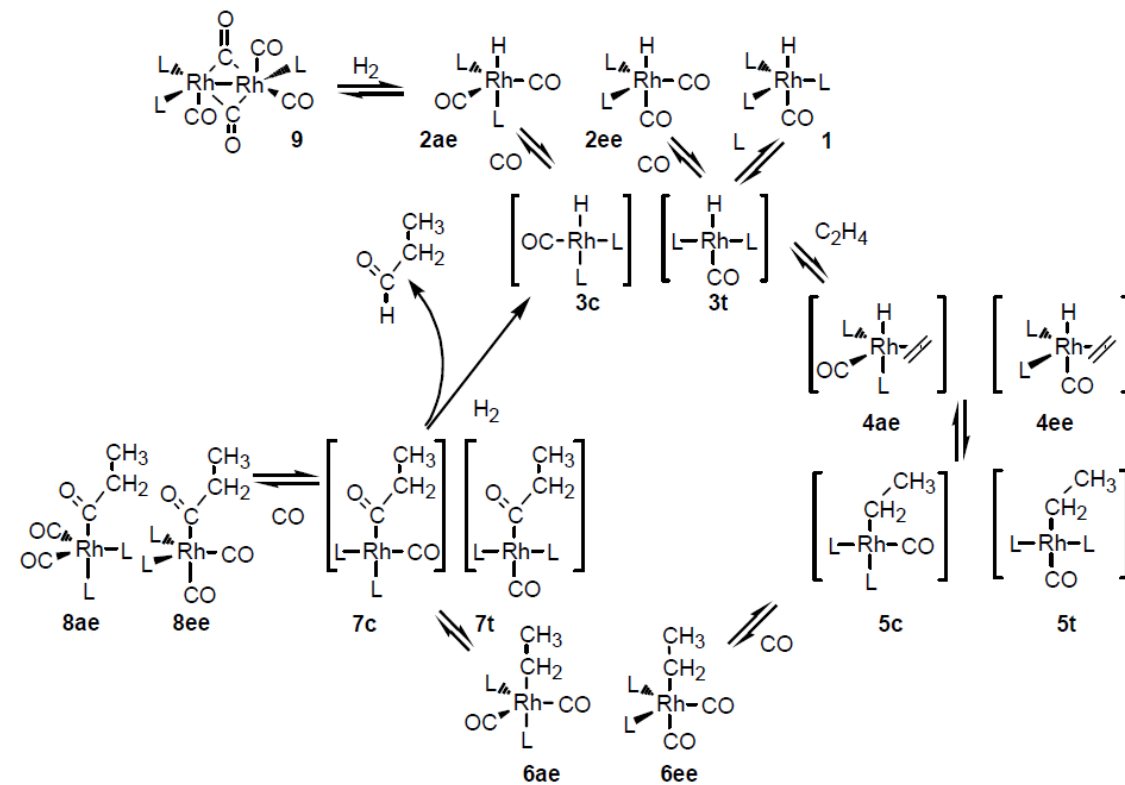
6.2.2 RHODIUM-CATALYZED HYDROFORMYLATION

The following rhodium catalyst containing the bidentate BISBI ligand has been shown to give extremely high linear to branched ratios in hydroformylation reactions. **Explain the origin of this phenomenon and design one or more experiments to test your reasoning.**





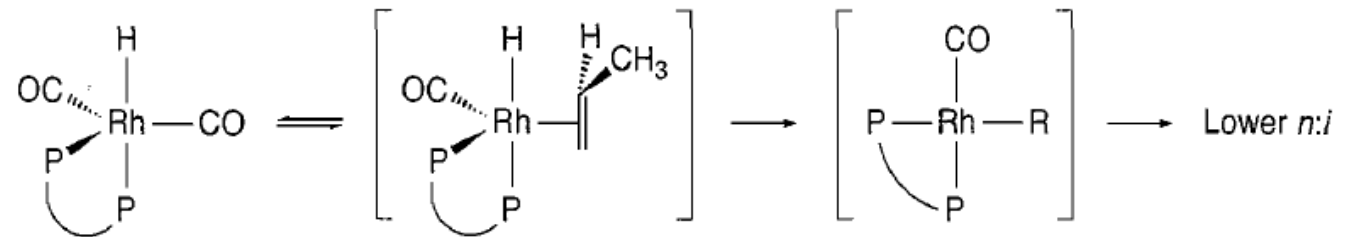
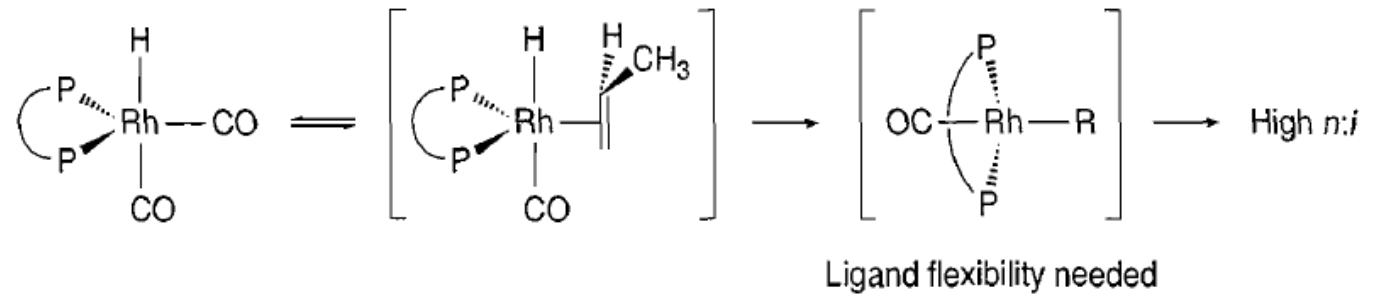
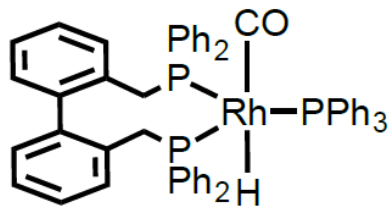
6.2.2 RHODIUM-CATALYZED HYDROFORMYLATION - MECHANISM





POD #3

The following rhodium catalyst containing the bidentate BISBI ligand has been shown to give extremely high linear to branched ratios in hydroformylation reactions. **Explain the origin of this phenomenon and design one or more experiments to test your reasoning.**





6.2.2 Rh-CATALYZED HYDROFORMYLATION - REGIOSELECTIVITY

